Effect of alternate CH_4-reducing/lean combustion treatments on the reactivity of fresh and S-poisoned $Pd/CeO_2/Al_2O_3$ catalysts

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Abstract

This work investigates the effect of treatments under different CH_4-containing atmospheres on the reactivity of fresh and S-poisoned 2% w/w $Pd/Al_2O_3/CeO_2$ catalysts for methane combustion.

Over the fresh catalyst the decomposition/reformation processes of PdO occurring during cycles of CH_4-reducing/lean combustion pulses allowed the complete recovery of activity losses possibly associated with H_2O poisoning which were observed during prolonged exposure under lean combustion conditions. The presence of CeO_2 markedly enhances both the activity losses under lean combustion conditions and the rate of PdO reoxidation/reactivation upon Pd redox cycle.

Under lean combustion conditions, regeneration of catalyst deactivated by exposure to SO_2-containing atmosphere required very high temperatures (above 750 °C) in order to decompose stable sulphate species adsorbed on the support. Treatments consisting of alternate CH_4-reducing/lean combustion pulses allowed a complete recovery of activity at much lower temperatures (550–600 °C) due to the reduction of sulphates by CH_4 activated on the surface of Pd metal. A protecting role of CeO_2 on Pd poisoning due either to exposure to SO_2-containing atmosphere or to spill-back of support sulphates species was also evidenced.
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1. Introduction

In the last decade an increasing attention has been devoted to natural gas fuelled vehicles (NGVs), appearing attractive to decrease pollution in the cities thanks to reduced emission of NO_x and particulate compared to diesel engines. This "green" image risks to be compromised by the unburned methane, a potent greenhouse gas, emitted in the exhausts. Accordingly, severe limitations on CH_4 emissions have been enforced [1]. In order to meet these severe regulations a catalytic exhaust converter must be installed on NGVs. Pd supported catalysts are widely recognized as the most active in combustion of methane at the low temperatures and CH_4 concentrations characteristic of this application [1–5]. Nevertheless the strong sensitivity of Pd supported catalysts to water and to sulphur-containing compounds represents a serious drawback to their use for exhaust after treatment [3,6–11].

As evidenced in several studies, the support markedly influences the rate of SO_2 poisoning of the PdO catalyst [3,12]. In particular a slower deactivation occurs in the presence of sulphating supports, such as Al_2O_3, which allow scavenging of sulphate species [3,12]. The rate of catalyst deactivation due to the exposure to SO_2-containing atmospheres is markedly influenced by modifications of catalyst formulation, such as the incorporation of oxides of transition metal (Ni, Cu) or rare earth (Ce, La) in alumina supports [13]. The interaction between SO_2 and CeO_2 has been widely investigated in literature, since CeO_2 is a well known promoter currently used in catalytic mufflers operating under alternate reducing and oxidizing environments [13–17]. Literature reports [13,18,19] evidenced an increase of SO_2 uptake on CeO_2 with respect to Al_2O_3, likely associated with the enhanced formation of surface and bulk sulphates [20] due to the higher basicity of CeO_2 [17]. Nevertheless no significant improvement in preserving catalyst activity was

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observed following doping Pd/Al_2O_3 by sulphating CeO_2 promoter [13,21].

A proposed strategy to face up deactivation due to SO_2 poisoning is represented by periodical short excursions to high temperature under lean or reducing atmosphere to favour the decomposition of sulphates species inhibiting catalyst activity [6,13,22]. In a previous work we observed that treatments under CH_4-reducing atmosphere are more effective in regeneration of S-poisoned Pd/Al_2O_3 than treatments under H_2-reducing or under CH_4-lean combustion atmospheres [22]. Short CH_4-reducing pulses led to partial reactivation of S-poisoned Pd/Al_2O_3 catalyst already at 550 °C and to practically complete regeneration at 600 °C following a marked SO_2 release due to the decomposition of stable support sulphates [22]. Moreover experiments performed over unpoisoned catalyst showed that PdO reduction/reformation processes occurring during alternate CH_4-reducing/CH_4-lean pulses result in a complete recovery of activity losses that were observed during prolonged exposure under lean combustion conditions, possibly associated with H_2O poisoning phenomena [22].

In this work the effect of pulse treatments on the regeneration of S-poisoned 2% w/w $Pd/Al_2O_3/CeO_2$ catalysts was investigated. In particular alternate pulse and temperature step experiments were carried out in order to individuate the temperature threshold to obtain catalyst reactivation under different CH_4-containing atmospheres: lean combustion (excess of O_2) and CH_4-reducing (O_2 free) conditions. The effect of alternate lean combustion/CH_4-reducing pulses over the unpoisoned catalyst was also addressed. The results are compared with those previously obtained over an unpromoted Pd/Al_2O_3 catalyst [22] aiming at understanding the effect of CeO_2 on: (i) the decomposition/reformation process of supported PdO and the related activity modifications in fresh catalyst; (ii) the regeneration behaviour of S-poisoned catalysts.

2. Experimental

A γ-Al_2O_3 (LaRoche Versal TD250) sample calcined at 1073 K for 6 h was used as starting material. The 15% w/w CeO_2-doped support was prepared by incipient wetness technique using $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich 99.99%) as precursor. The support was dried overnight at 393 K and calcined at 1273 K for 6 h under air flow. The BET surface area of the support upon calcination was 123 m^2/g.

2% w/w Pd was loaded in a single step by incipient wetness using an aqueous solution of $Pd(NO_3)_2$ (Aldrich, 10% w/w Pd, 99.999%). Then, the catalyst was dried overnight at 393 K and calcined for 6 h at 1073 K in a 0.2 l/min air flow (heating/cooling rate 10 °C/min). The final BET surface area of the catalyst was 98 m^2/g.

Fresh catalyst was submitted to an accelerated SO_2 poisoning treatment performed at 380 °C for 15 h in a stream containing 10 ppm SO_2, 0.5% CH_4, 2% O_2, He to balance, at GHSV = 180,000 cm^3/(g h) at STP, in presence of water as a product of CH_4 combustion. The poisoning procedure resulted in adsorption of 3.3 μmol/m^2 of SO_2, a similar

amount to that observed over Pd/Al_2O_3 (3.9 μmol/m^2), associated with a marked decrease of CH_4 conversion. FT-IR characterization confirmed that sulphation occurred via chemisorption of OH groups. Evidences for surface and bulk CeO_2 sulphates were found [20]. Further details on procedure and poisoning behaviour will be reported on a forthcoming paper [21].

Fresh and poisoned catalysts were tested in the form of fine powders (d_p = 0.72 μm) loaded in a microreactor (60 mg) with a 1/1 catalyst/inert quartz dilution ratio. m/e signals corresponding to H_2 (2), CH_4 (15), O_2 (32), H_2S (34), Ar (40), CO_2 (44), SO_2 (64), were collected. The 28 m/e signal was also recorded, but quantification was not possible due to overlapping of N_2 and CO response. Temperature was measured by a K-type thermocouple placed in the catalyst bed. Further details on the test rig were reported in Ref. [22].

2.1. Fresh catalyst

Wet CH_4-TPR (Temperature Programmed Reduction) tests were carried out feeding the reactor with 0.5% CH_4, 16% N_2, 2% H_2O, balance He at 150 cm^3/min at STP corresponding to GHSV = 150,000 N cm^3/(g h). Temperature was ramped at 15 °C/min up to 500 °C and the catalyst was cooled at the same rate down to room temperature.

The behaviour of fresh catalyst at a constant temperature of 350 °C was investigated also by means of experiments consisting of a series of alternate: (i) CH_4-reducing (0.5% CH_4, 2% H_2O, balance He–Ar tracer) and lean combustion (0.5% CH_4, 4% O_2, 16% N_2, 2% H_2O, balance He–Ar) pulses; (ii) alternate CH_4-reducing (0.5% CH_4, 2% H_2O, balance He–Ar tracer)/dry oxidizing (4% O_2, 16% N_2, balance He)/lean combustion (0.5% CH_4, 4% O_2, 16% N_2, 2% H_2O, balance He–Ar) pulses; (iii) alternate CH_4-reducing (0.5% CH_4, 2% H_2O, balance He–Ar tracer)/wet oxidizing (4% O_2, 16% N_2, 2% H_2O, balance He)/lean combustion (0.5% CH_4, 4% O_2, 16% N_2, 2% H_2O, balance He–Ar) pulses. H_2O was always added in the feed, unless differently specified (dry conditions), in view of its strong influence on Pd catalyst performances.

Alternate pulse experiments were performed according to the following procedure. The catalyst was maintained for 30–60 min under lean combustion conditions, then the feed was switched to pure He for 40–50 s to favour the desorption of species adsorbed on catalyst surface and the purge of the dead volume. After the purge a CH_4-reducing stream was fed to the reactor for 2 min and subsequently a helium purge was again carried out for 40–50 s. Finally depending on the type of the experiment the reactor was fed by: (i) a lean combustion flow for 40 min; (ii) the dry oxidizing stream for 10 min followed by the lean combustion flow for 30 min; (iii) the wet oxidizing stream for 10 min followed by the lean combustion flow for 30 min. Ar tracer was always co-fed with CH_4 (CH_4/Ar = 10) to clearly identify the actual switch time between different atmospheres. During all the different phases the flow rate was kept at 150 cm^3/min at STP corresponding to a GHSV = 150,000 N cm^3/(g h).
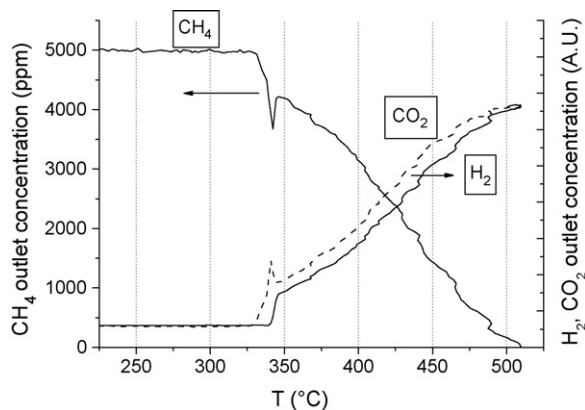
Fig. 1. CH_4, H_2 and CO_2 outlet concentration during wet CH_4-TPR tests over fresh $Pd/Al_2O_3/CeO_2$ catalyst.

2.2. S-poisoned catalyst

Wet CH_4-TPR experiments were performed using the same feed and GHSV reported for the fresh catalyst. Temperature was ramped up and down from RT to 900 °C at 15 °C/min.

Two types of temperature step experiments were performed to investigate the regeneration behaviour of the S-poisoned catalyst. CH_4 conversion value under lean combustion conditions at 400 °C was initially registered. Temperature was then increased by 50 °C steps at 15 °C/min up to different levels: 450 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, 750 °C and 800 °C. After each temperature step the catalyst was cooled down to 400 °C and CH_4 conversion was measured again under standard lean combustion conditions so as to evaluate activity differences by comparison with the conversion determined at the beginning of the experiment. Two types of treatments were performed at each temperature step: (i) 1 h aging under lean combustion conditions (0.5% CH_4, 4% O_2, 16% N_2, 2% H_2O, balance He–Ar); (ii) a series of four alternate CH_4-reducing (0.5% CH_4, 2% H_2O, balance He–Ar)/lean combustion (0.5% CH_4, 4% O_2, 16% N_2, 2% H_2O, balance He–Ar) pulses. Alternate pulse experiments were performed according to the same procedure illustrated for the fresh catalyst.

## 3. Results and discussion

3.1. Fresh catalyst

3.1.1. TPR experiments

The results of wet CH_4-TPR experiments performed over the fresh catalysts are shown in Fig. 1. Consumption of CH_4 was registered between 325 °C and 345 °C accompanied by a peak of CO_2 outlet concentration associated with reduction of PdO to Pd by CH_4. At higher temperatures a marked CH_4 consumption was observed, accompanied by production of CO_2, CO (not reported in the graph because of quantification problems) and H_2 likely associated with steam reforming and shift reactions occurring over metallic Pd.

3.1.2. Alternate pulse experiments

Following the results obtained by Bell and coworkers [23] over a 10% w/w Pd/ZrO_2 catalyst and confirmed in a previous work performed in our laboratory over 2% w/w Pd/Al_2O_3 [22], fresh catalysts were submitted to several cycles of alternate CH_4-reducing/lean combustion pulse experiments at 350 °C before achieving a stable behaviour. During such stabilization treatment CH_4 conversion at 350 °C under lean combustion conditions increased from 15% to 40%.

Fig. 2 shows profiles of CO_2 and H_2 outlet concentrations obtained in one cycle of alternate reducing/lean combustion pulses performed over the unpoisoned $Pd/Al_2O_3/CeO_2$ catalyst after stabilization. Under lean combustion conditions oxidation of CH_4 occurred, reaching almost 40% conversion, only CO_2 and H_2O being detected in the effluent. When switching to the CH_4-reducing pulse an initial sharp peak in CO_2 concentration was observed. This trend was consistent with the reduction of PdO to metallic Pd by CH_4 according to the following stoichiometry:

$$CH_4 + 4PdO \rightarrow CO_2 + 2H_2O + 4Pd \qquad (1)$$
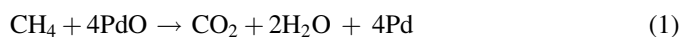
as confirmed by quantitative evaluation of CH_4 consumption and CO_2 release. A significant contribution of CO_2 desorption from the catalyst surface can be excluded since no evolution of this species was detected during the He purge. Subsequently, upon formation of Pd metal, H_2 production started and a plateau value in CO_2 outlet concentration was reached likely associated
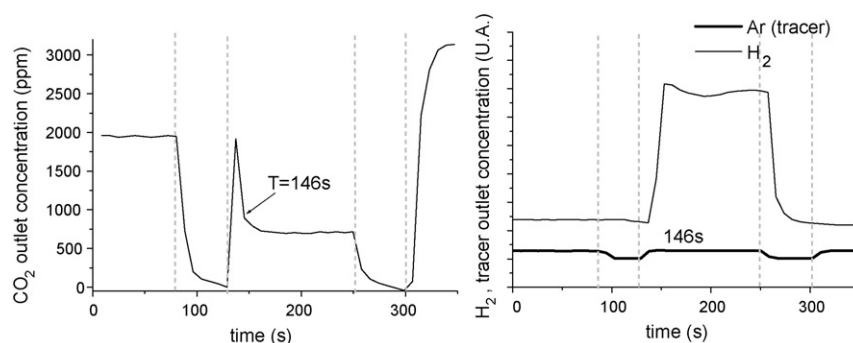

Fig. 2. CO_2 (left panel) and H_2 (right panel) outlet concentrations during alternate lean combustion/reducing pulses at 350 °C over unpoisoned $Pd/Al_2O_3/CeO_2$ catalyst after stabilization. Vertical dashed lines correspond to atmosphere switch.
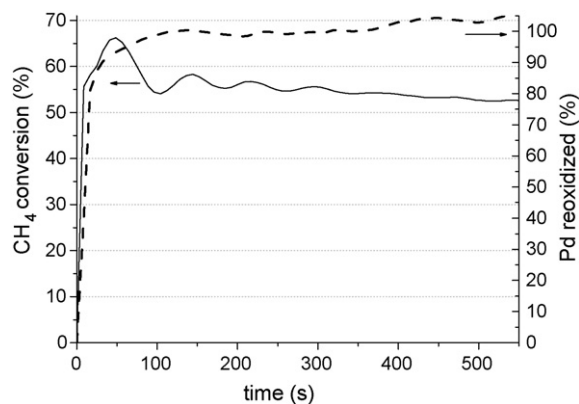
Fig. 3. Comparison of time evolution of CH_4 conversion at 350 °C after restoring lean combustion conditions (solid line) with % of Pd reoxidation evaluated from O_2 uptake (dashed line) over unpoisoned $Pd/Al_2O_3/CeO_2$.

Fig. 4. CH_4 conversion during a sequence of alternate CH_4-reducing/lean combustion pulses at 350 °C over unpoisoned $Pd/Al_2O_3/CeO_2$ catalyst after stabilization.

with steam reforming and shift reactions [24]. Such a value was significantly higher than that observed over the unpromoted Pd/Al_2O_3 catalyst under similar conditions [22], in line with the promoting effect of CeO_2 on shift and steam reforming reactions [25].

When lean combustion conditions were restored after the reducing pulse the catalyst underwent to a fast reactivation during the first 50 s reaching a maximum of 65% CH_4 conversion (Fig. 3 solid line). A significant deactivation down to 55% conversion was observed in the following 50–60 s and then a more gradual decrease of conversion occurred. In Fig. 3 such conversion trend is compared with the cumulative oxygen uptake registered during an oxidizing CH_4-free pulse performed after the reducing pulse. The fast increase in methane conversion observed during the first 50 s after restoring oxidizing conditions was paralleled by a fast rate of oxygen consumption, leading to a stationary value in the cumulative oxygen uptake, which reasonably corresponded to the theoretical amount associated with the complete reoxidation of Pd. Such data confirmed that palladium oxide progressively formed under oxygen-rich atmospheres is the active phase in CH_4 combustion at low temperatures, while the metallic state obtained upon reducing pulse is poorly active [1,2 and references therein].

It is worth noting that in the presence of CeO_2 the reactivation was markedly faster with respect to that observed over an undoped 2% w/w Pd/Al_2O_3 under similar conditions (50 s vs. 300 s to complete the reactivation) [22]. This confirmed a role of CeO_2 as a promoter of Pd reoxidation, which has been already reported in the literature [26–28].

In Fig. 4 is reported the behaviour of the unpoisoned $Pd/Al_2O_3/CeO_2$ catalyst during repeated cycles of alternate CH_4-reducing/lean combustion pulses performed after stabilization. The catalyst showed a very reproducible activity trend. Following the initial peak of 65% CH_4 conversion, already illustrated in Fig. 3, a progressive loss of activity was registered during prolonged exposure under lean combustion conditions corresponding to a 15–20% decrease of CH_4 conversion during 40 min. The activity was completely restored upon a CH_4-reducing pulse and the following Pd reactivation/reoxidation
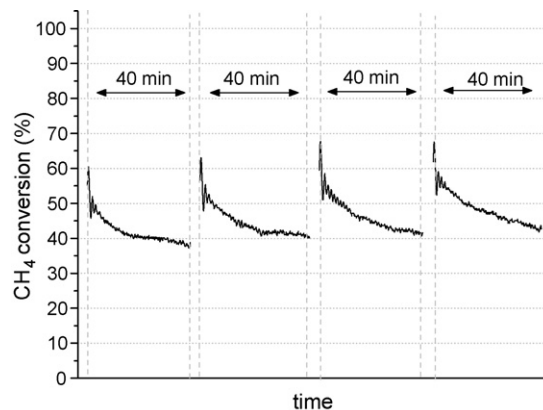
process under lean combustion atmosphere. The undoped Pd/Al_2O_3 catalyst submitted to a similar treatment showed a much slower deactivation rate, passing from 55% to nearly 50% methane conversion after 30–60 min under lean combustion conditions [22]. Similar deactivation trends were observed also by Yu Yao [29] during experiments of C_4H_{10} oxidation over Pd/Al_2O_3 and $Pd/Al_2O_3/CeO_2$. Such behaviour was ascribed to a progressive reoxidation of metal Pd to a less active PdO form upon exposure to O_2 rich conditions after the reducing pulse. Results obtained in this work seem to exclude this hypothesis, since complete reoxidation of Pd to PdO apparently occurred at much shorter times than those characteristics of catalyst deactivation. To better address this point further experiments with alternate CH_4-reducing/dry or wet oxidizing/lean combustion pulses were performed. The results are reported in Fig. 5: (1) as already shown in Fig. 4, under lean combustion conditions at 350 °C following a reducing pulse a value of about 65% CH_4 conversion was initially registered, which gradually decreased down to 50%; (2) when restoring lean combustion conditions upon a reducing pulse followed by 10 min of dry oxidizing stream which resulted in complete Pd reoxidation, a
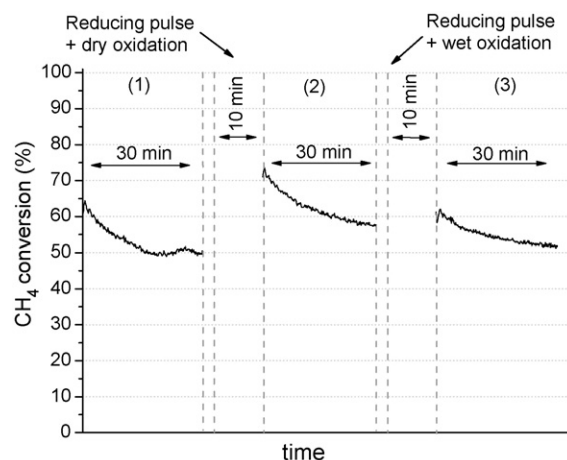

Fig. 5. CH_4 conversion at 400 °C under lean combustion conditions during alternate lean combustion/CH_4-reducing/wet (or dry) oxidizing pulse experiments.
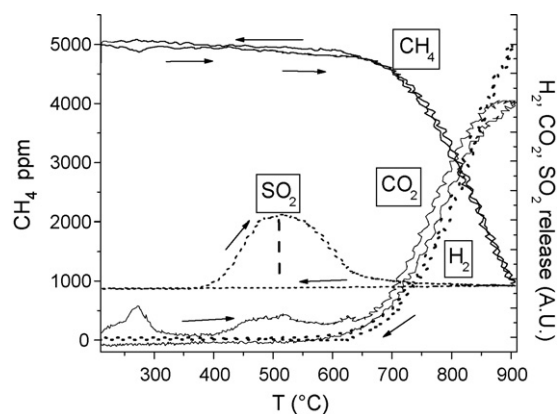
Fig. 6. CH_4, H_2, CO_2 and SO_2 outlet concentration during wet CH_4-TPR tests over S-poisoned $Pd/Al_2O_3/CeO_2$ catalyst.

Fig. 7. CH_4 conversion at 400 °C over the S-poisoned $Pd/Al_2O_3/CeO_2$ after steps at different temperatures under lean combustion condition. CH_4 conversion over the unpoisoned $Pd/Al_2O_3/CeO_2$ catalyst under the same conditions is reported for the sake of comparison (dotted line).

value of 75% CH_4 conversion was registered followed by a decrease down to nearly 60%; (3) on the other hand upon a reducing pulse followed by reoxidation under wet oxidizing conditions a 60% CH_4 conversion value was observed and then a more gradual decrease down to 50% was registered during 30 min. It was evident that complete oxidation under dry conditions resulted in high CH_4 combustion activity whereas oxidation in the presence of water markedly affected the performances of PdO catalyst. Although alternative explanation such as progressive saturation of vacancies on PdO surface [30] cannot be excluded, these results suggest that H_2O could play a major role on the deactivation occurring during prolonged exposure under lean combustion conditions in line with many literature reports [4,5,31–34]. The deactivation could be associated with different phenomena including formation of inactive $Pd(OH)_2$ species [31], smoothening of PdO crystallites with decrease of active surface [32], and sintering of palladium particles [4]. However such deactivation was completely reversible upon a reduction/reoxidation cycle which may results in decomposition of $Pd(OH)_2$ and/or in roughening of the newly formed PdO surface [31].

3.2. S-poisoned catalyst

3.2.1. TPR experiments

As shown in Fig. 6, during a wet CH_4-TPR test over the S-poisoned catalyst, a pronounced peak of SO_2 release associated with decomposition of sulphates was detected between 400 °C and 700 °C. A small peak of CO_2 production was observed in the temperature range 250–300 °C, which was accompanied by a slight CH_4 consumption. This peak was associated with the partial reduction of PdO to Pd, occurring at lower temperature over the S-poisoned catalyst than over the fresh one. Noteworthy the T-threshold of PdO reduction in wet CH_4-TPR test over the S-poisoned catalyst compared well with that observed in dry TPR experiments (not reported) over the fresh catalyst suggesting that the increase of the support acidity associated with the presence of sulphates might prevent H_2O inhibition on the partial reduction of PdO. However, differently from the TPR profile of the unpoisoned catalyst (Fig. 1) no evidences of CH_4 reforming/decomposition reactions (CH_4
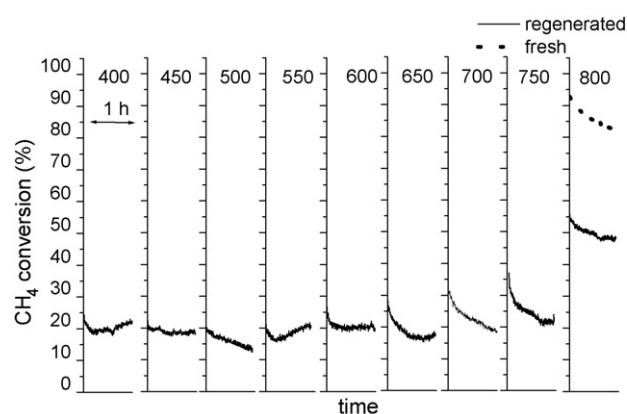
consumption accompanied by CO_2 and H_2 production) were observed upon the first reduction peak. A marked decrease of CH_4 outlet concentration was progressively evident only above 650 °C, i.e. after extensive catalyst desulphation, which was paralleled by an increase of CO_2, and H_2 outlet concentrations likely due to steam reforming, water gas shift and, possibly, CH_4 decomposition reactions occurring at high temperature over metallic Pd. This is in line with the preferential block by S-poisoning of the steam reforming reaction with respect to oxidation reactions already observed in the literature over noble metal catalysts [35]. Above 700 °C, following a significant H_2 production, a slight H_2S release was registered (not shown in the figure), which was associated with the reduction of sulphates to sulphides in line with literature reports [14].

3.2.2. Temperature step experiments

In Fig. 7 are reported the results of temperature step experiments under lean combustion conditions performed over S-poisoned $Pd/Al_2O_3/CeO_2$. A slight reactivation was observed only above 700 °C. Upon heating the catalyst up to 800 °C a value of 50% CH_4 conversion was registered at 400 °C, to be compared with 90% conversion obtained at the same temperature over the fresh catalyst after stabilization. This
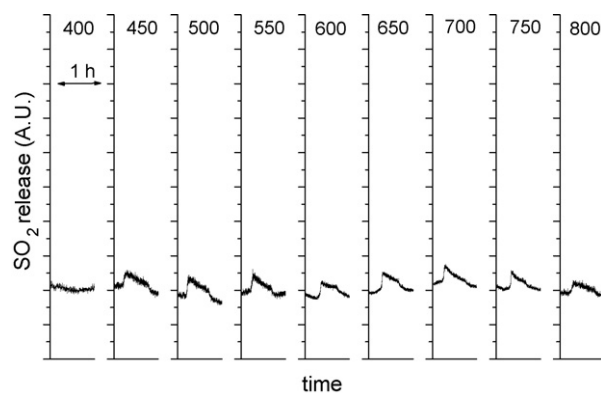

Fig. 8. Profiles of SO_2 release during temperature steps experiments under lean combustion conditions.
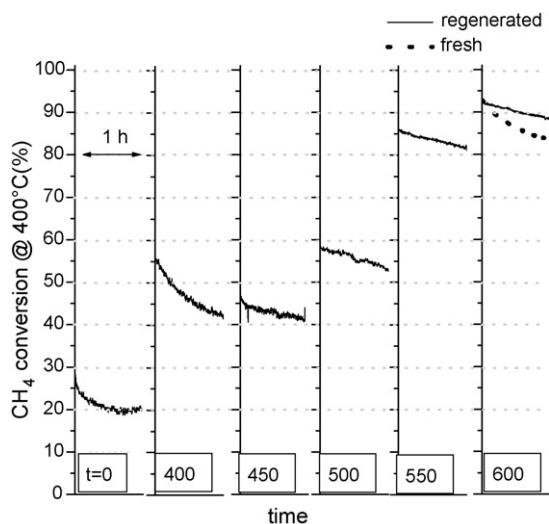
Fig. 9. CH_4 conversion under lean combustion conditions at 400 °C over the S-poisoned $Pd/Al_2O_3/CeO_2$ catalyst after cycles of four alternate CH_4-reducing lean combustion pulses at different temperature steps. CH_4 conversion over the unpoisoned $Pd/Al_2O_3/CeO_2$ catalyst under the same conditions is reported for the sake of comparison (dotted line).

the activity recovery is prevented due to spill-back of more stable sulphate species from the support to the active sites [3,22]. Accordingly reactivation was reached only following further decomposition of more stable support sulphates, which occurred above 700 °C. It is worth noting that the extent of the regeneration at 800 °C was significantly lower than that observed on the unpromoted Pd/Al_2O_3 catalyst [22], possibly due to the presence of more stable sulphates associated with the basicity of ceria [16,17].

CH_4 conversion at 400 °C obtained under lean conditions upon cycles of alternate-reducing/lean combustion pulses at different temperature is shown in Fig. 9. The curve at $t = 0$ corresponds to initial catalyst activity before any reducing pulse. CH_4 conversion increased from 20% up to 45% just upon one CH_4-reducing pulse of 2 min at 400 °C. Cycles of alternate CH_4-reducing/lean combustion pulses at 450 °C did not result in any further activity increase, whereas after treatments at 500 °C and 550 °C a marked catalyst reactivation was observed. Complete regeneration leading to 90% CH_4 conversion in lean combustion at 400 °C was obtained upon reducing pulses at 600 °C, as evidenced by comparison with the performances of the fresh catalyst under the same conditions.

The outlet concentration of SO_2 and CO_2 observed during the first reducing pulse performed at each temperature level are reported in Fig. 10. The results obtained in identical experiments performed over Pd/Al_2O_3 catalyst [22] are also reported for the sake of comparison. At 400 °C a pronounced CO_2 peak was observed in the CeO_2 promoted sample, accompanied by a marked decrease of CH_4 concentration (not shown in the figure) while no SO_2 release was registered.

indicates that a significant, but not complete, regeneration occurred. In Fig. 8 the SO_2 release registered at each temperature is reported. A slight SO_2 release was observed also during steps at temperatures between 450 °C and 650 °C, whereas no activity recovery was measured. This behaviour is consistent with literature reports indicating that decomposition of Pd sulphates can occur already below 700 °C [3,12,22], but
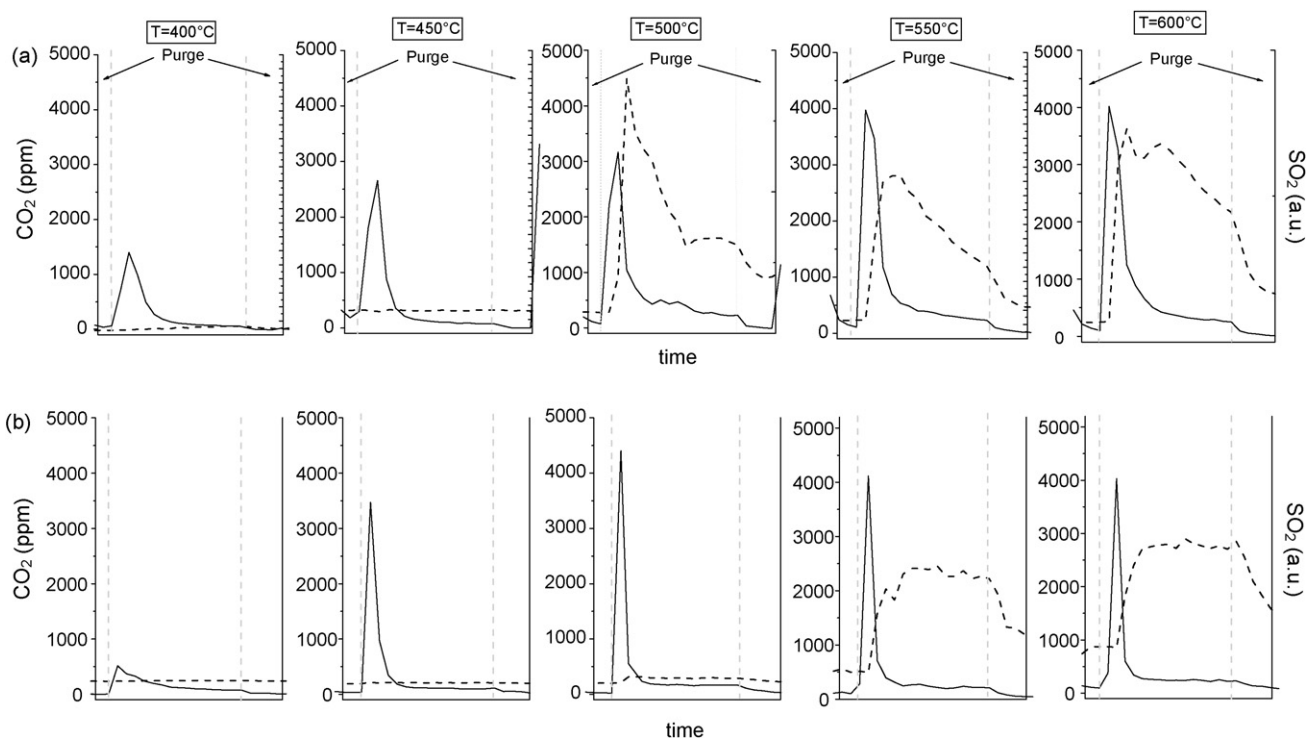

Fig. 10. Profiles of SO_2 (dashed lines) and CO_2 (solid lines) outlet concentration during the 1st CH_4-reducing pulses and the following He purge at each temperature step. (a) $Pd/Al_2O_3/CeO_2$; (b) Pd/Al_2O_3 (data from Ref. [22]).

Quantitative evaluations of CO_2 production and CH_4 consumption were consistent with the reduction of about 1/3 PdO load to metal Pd according with the stoichiometry (1). Also at 450 °C a marked CO_2 production was observed whereas SO_2 release was still not detected. At 500 °C an even more pronounced CO_2 peak occurred, indicating that PdO underwent to almost complete reduction. At this temperature a marked SO_2 desorption was detected upon the formation of Pd metal. At 550 °C and 600 °C a CO_2 peak corresponding to the complete reduction of PdO was observed followed by a pronounced SO_2 release.

The behaviour showed by $Pd/Al_2O_3/CeO_2$ during pulses at temperatures higher than 500 °C was similar to that observed in analogous experiments performed over unpromoted Pd/Al_2O_3 [22]. According to the mechanism proposed therein, the SO_2 release observed starting from 500 °C is associated with the reduction of the stable sulphates species by CH_4 activated on the pre-reduced Pd metal surface. The extended desulphation of the support promoted by CH_4-reducing treatments resulted in the recovery of catalyst activity. Noteworthy over $Pd/Al_2O_3/CeO_2$ the SO_2 release has been registered already at 500 °C, about 50 °C below the temperature required over the undoped Pd/Al_2O_3 [22], suggesting a promoting effect of CeO_2 in the reduction of sulphates.

The behaviour of $Pd/Al_2O_3/CeO_2$ during CH_4-reducing pulses at low temperature was quite different from that of the undoped Pd/Al_2O_3. In the case of Pd/Al_2O_3 no catalyst reactivation was detected at 400 °C along with a very small CO_2 peak and the absence of SO_2 desorption [22]. On the other hand in the case of $Pd/Al_2O_3/CeO_2$, at the same temperature a pronounced peak of CO_2 was detected, in line with the results of wet CH_4-TPR experiments, and a marked catalyst reactivation was observed although no SO_2 release occurred. Such CO_2 pronounced peak likely indicates that even after prolonged exposure to SO_2-containing atmosphere a certain amount of PdO was still unpoisoned and could be reduced to Pd, suggesting that CeO_2 can partly protect PdO from sulphation. As shown over the unpoisoned catalyst, the reduction/reoxidation cycle of PdO can account for the partial recovery of activity observed already at 400 °C.

Noteworthy at 450 °C a significant CO_2 peak was observed also over Pd/Al_2O_3 still without any SO_2 release and no catalyst reactivation. This was explained suggesting that at this temperature CH_4 was able to partly remove labile Pd surface sulphates so to allow for partial reduction of PdO, but reactivation upon restoring lean combustion conditions was prevented by spill-back of stable sulphates from the support. Accordingly the reactivation observed over $Pd/Al_2O_3/CeO_2$ at low temperatures when support sulphates are not yet decomposed, also suggests that CeO_2 could hinder the spill-back of sulphates occurring when feed is switched from reducing pulse to lean combustion conditions.

The results indicate that the protecting effect of CeO_2 on Pd sulphation both from gaseous SO_2 and from spill-back of support sulphates could be effective only on a fraction of palladium. Indeed despite of the marked CO_2 release at 450 °C no further reactivation of the CeO_2 promoted sample was observed before extensive decomposition of support sulphates occurring at higher temperature. This indicates that the additional fraction of palladium, which underwent to redox cycle at 450 °C was deactivated by sulphate spill-over upon restoring lean combustion conditions. In a previous investigation [28] on a catalyst with similar composition ($3\%Pd/10\%CeO_2/Al_2O_3$) it was shown by HRTEM and TPO experiments that only a fraction of Pd particles is in direct contact with CeO_2 crystallites, and this contact is necessary for ceria in order to promote Pd reoxidation. Along these lines it can be hypothesised that direct contact of CeO_2 with palladium particles is required to provide protection from sulphation.

Finally it is worth noting that the protecting effect of CeO_2 on S-poisoning during treatment under CH_4 combustion atmosphere containing SO_2 was likely masked by the more pronounced effect of H_2O poisoning discussed above. As a result Pd/Al_2O_3 and $Pd/Al_2O_3/CeO_2$ showed comparable deactivation levels upon such treatments [21].

Noticeably neither H_2 nor H_2S production was detected during CH_4-reducing pulses up to 600 °C under conditions adopted in our experiments. This was in line with the results of wet CH_4-TPR showing a preferential poisoning of steam reforming reaction. Several studies observed that H_2S production occurs during reduction under H_2-containing atmosphere and is accompanied by degradation of catalyst performances likely due to the formation of surface metal sulphides [9,12,22] or to the formation of cerium sulphides [14,36] which can be reoxidized to sulphates under lean combustion conditions and prevent a complete recovery of activity due to the spill-back of sulphate species to Pd surface [3]. In line with previous results obtained over S-poisoned Pd/Al_2O_3 [22], the experiments performed in this work over $Pd/Al_2O_3/CeO_2$ catalyst evidenced that sulphate species inhibiting catalyst activity can be effectively removed from the support by treatment at 500–600 °C under CH_4-reducing conditions resulting in a complete recovery of activity, indicating that the milder reducing strength of CH_4 with respect to H_2 [32] can hinder the formation of sulphides. This is in line with the results of Beck et al. [13], who observed a complete activity recovery for S-poisoned $Pd/Al_2O_3/CeO_2$ catalyst upon treatment above 650 °C under mild reducing propene-rich atmosphere.

4. Conclusions

By comparing the results of alternate CH_4-reducing/lean combustion pulses and temperature step experiments performed over fresh and S-poisoned $Pd/Al_2O_3/CeO_2$ with those obtained in a previous work over an undoped Pd/Al_2O_3 system the following conclusions can be drawn:

Over the unpoisoned catalysts prolonged exposure to lean combustion atmosphere results in significant activity losses, which are more pronounced in the presence of CeO_2 and are possibly associated with H_2O poisoning phenomena. Such deactivation is completely reversible following a PdO reduction/reoxidation cycle associated with alternate CH_4-reducing/lean combustion pulses.

The reactivation observed upon restoring lean combustion conditions after the reducing pulse is associated with Pd reoxidation and is markedly faster in the CeO_2-doped catalyst with respect to the undoped Pd/Al_2O_3, confirming that CeO_2 acts as a promoter of Pd reoxidation.

Over the S-poisoned catalysts reactivation under lean combustion conditions requires very high temperatures ($>750\ ^{\circ}C$), which are necessary to thermally decompose stable sulphates adsorbed on the support.

CH_4-reducing pulses allow to obtain catalyst reactivation at much lower temperatures (550–600 $^{\circ}C$) due to reduction of sulphates by CH_4 activated onto Pd metal surface. In the CeO_2 promoted catalyst the reduction of sulphates is slightly anticipated.

In the presence of CeO_2 a partial reactivation was observed already upon a CH_4-reducing pulse at 400 $^{\circ}C$. Such reactivation, which was not observed over Pd/Al_2O_3, is likely due to reduction/reformation processes of unpoisoned PdO. This indicates that CeO_2 may prevent S-poisoning of a certain amount of PdO both during exposure to SO_2-containing atmospheres and from spill-back of support sulphates.

The results collected in this work confirmed that regeneration of S-poisoned catalysts with CH_4-reducing stream is more effective than analogous treatment under H_2-containing atmosphere.

Acknowledgment

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